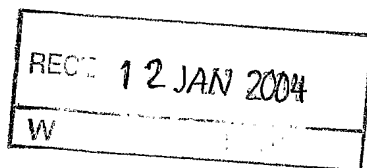




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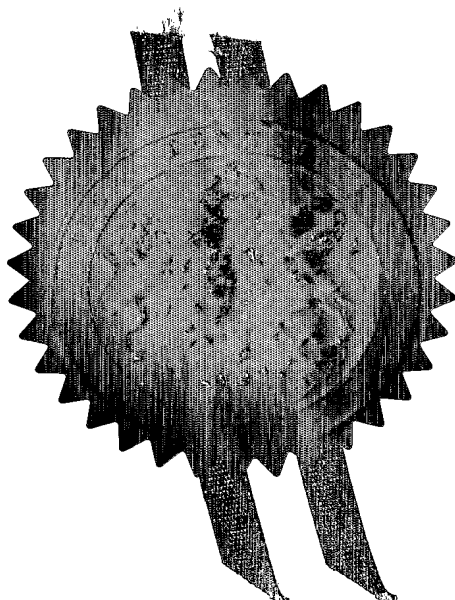
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28 NOV 2002  
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Patents ADP number (if you know it) 06166441006

If the applicant is a corporate body, give the country/state of its incorporation United Kingdom

4. Title of the invention Droplet - Deposition related methods and apparatus

5. Name of your agent (if you have one)  
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- a) any applicant named in part 3 is not an inventor, or
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## DROPLET - DEPOSITION RELATED METHODS AND APPARATUS

This invention generally relates to the deposition of material for electronic devices, particularly molecular electronic devices such as organic light emitting diodes, by an ink jet-type process. The invention is particularly concerned with droplet volume measurement and calibration techniques and droplet-based deposition methods.

Organic light emitting diodes (OLEDs) comprise a particularly advantageous form of electro-optic display. They are bright, colourful, fast-switching, provide a wide viewing angle and are easy and cheap to fabricate on a variety of substrates. Organic LEDs may be fabricated using either polymers or small molecules in a range of colours (or in multi-coloured displays), depending upon the materials used. Examples of polymer-based organic LEDs are described in WO 90/13148, WO 95/06400 and WO 99/48160; examples of so called small molecule based devices are described in US 4,539,507.

A basic structure 100 of a typical organic LED is shown in Figure 1a. A glass or plastic substrate 102 supports a transparent anode layer 104 comprising, for example, indium tin oxide (ITO) on which is deposited a hole transport layer 106, an electroluminescent layer 108, and a cathode 110. The electroluminescent layer 108 may comprise, for example, a PPV (poly(p-phenylenevinylene)) and the hole transport layer 106, which helps match the hole energy levels of the anode layer 104 and electroluminescent layer 108, may comprise, for example, PEDOT:PSS (polystyrene-sulphonate-doped polyethylene-dioxythiophene). Cathode layer 110 typically comprises a low work function metal such as calcium and may include an additional layer immediately adjacent to the electroluminescent layer 108, such as a layer of aluminium, for improved electron energy level matching. Contact wires 114 and 116 to the anode and the cathode respectively provide a connection to a power source 118. The same basic structure may also be employed for small molecule devices.

In the example shown in Figure 1a light 120 is emitted through transparent anode 104 and substrate 102 and such devices are referred to as "bottom emitters". Devices which emit through the cathode may also be constructed, for example by keeping the thickness of cathode layer 110 less than around 50-100 nm so that the cathode is substantially transparent.

Organic LEDs may be deposited on a substrate in a matrix of pixels to form a single or multi-colour pixellated display. A multicoloured display may be constructed using groups of red, green, and blue emitting pixels. In such displays the individual elements are generally addressed by activating row (or column) lines to select the pixels, and rows (or columns) of pixels are written to, to create a display. So-called active matrix displays have a memory element, typically a storage capacitor and a transistor, associated with each pixel whilst passive matrix displays have no such memory element and instead are repetitively scanned, somewhat similarly to a TV picture, to give the impression of a steady image.

Figure 1b shows a cross section through a passive matrix OLED display 150 in which like elements to those of Figure 1a are indicated by like reference numerals. In the passive matrix display 150 the electroluminescent layer 108 comprises a plurality of pixels 152 and the cathode layer 110 comprises a plurality of mutually electrically insulated conductive lines 154, running into the page in Figure 1b, each with an associated contact 156. Likewise the ITO anode layer 104 also comprises a plurality of anode lines 158, of which only one is shown in Figure 1b, running at right angles to the cathode lines. Contacts (not shown in Figure 1b) are also provided for each anode line. An electroluminescent pixel 152 at the intersection of a cathode line and anode line may be addressed by applying a voltage between the relevant anode and cathode lines.

It is known to deposit material for organic light emitting diodes (OLEDs) using ink jet printing techniques. This is described in, for example, T.R. Hebner, C.C. Wu, D. Marcy, M.H. Lu and J.C. Sturm, "Ink-jet Printing of doped Polymers for Organic Light Emitting Devices", *Applied Physics Letters*, Vol. 72, No. 5, pp.519- 521, 1998; Y. Yang, "Review of Recent Progress on Polymer Electroluminescent Devices," *SPIE Photonics West: Optoelectronics '98*, Conf. 3279, San Jose, Jan., 1998; EP O 880 303;

and "Ink-Jet Printing of Polymer Light-Emitting Devices", Paul C. Duineveld, Margreet M. de Kok, Michael Buechel, Aad H. Sempel, Kees A.H. Mutsaers, Peter van de Weijer, Ivo G.J. Camps, Ton J.M. van den Biggelaar, Jan-Eric J.M. Rubingh and Eliav I. Haskal, Organic Light-Emitting Materials and Devices V, Zakya H. Kafafi, Editor, Proceedings of SPIE Vol. 4464 (2002). Ink jet techniques can be used to deposit materials for both small molecule and polymer LEDs, although these applications present their own particular problems, which are different to the problems encountered in conventional ink jet printing of images on paper or plastic, as will be explained more fully below.

Use of an ink jet printer to deposit red, green and blue colour filters for a liquid crystal display or electroluminescent materials for an electroluminescent display is described in EP 1,219,980A. A similar technique is described in US 2002/0105688. Figures 2a and 2b, which are taken from EP '980, show ink jet printing apparatus which may be employed for this type of application. Figure 2a shows an ink jet printer 200 comprising a base 209 supporting first and second linear positioners 206, 208 for moving a substrate 212 and ink jet print head 222 relative to one another along two orthogonal axis Y and X. Positioner 206 comprises a pair of rails 254 mounting a slider 256 provided with a turntable 251 supporting a table or bed 249 on which the substrate 212 is supported. The substrate 212 is aligned on table or bed 249 by means of stops 250 against which two edges of the substrate abut. Turntable 251 allows the table and substrate 249, 212 to be rotated relative to the print head 222.

Positioner 208 comprises a pair of rails 252 mounting a slider 253 which carries rotary positioners 244, 246, 247 which allow a print head unit 226 carrying the print head to be rotated independently about three orthogonal axes. A further linear positioner 248 is also mounted on slider 253 to allow the print head unit and print head to be translated in the Z-direction, that is towards and away from substrate 212.

Ink jet printer system 200 is controlled by a computer terminal 202 via an umbilical 204. Terminal 202 may comprise a general purpose computer with interface hardware for interfacing to the above-described linear and rotary positioners, running operating system, user interface and other ink jet printer drive and control software, in a

conventional manner. Thus terminal 202 typically includes a data input device such as a network interface or floppy disk drive for receiving data defining a pattern to be printed, and printer control software to control the printer hardware to print a pattern in accordance with stored or input data. Other conventional functions such as test functions, head cleaning functions and the like are generally also provided by software running on terminal 202.

Figure 2b shows print head 222 in more detail. The print head has a plurality of nozzles 227, typically orifices in a nozzle plate for ejecting droplets of fluid from the print head onto the substrate. A fluid supply for printing (not shown in Figure 2b) may either be provided by a reservoir within the print head or print head unit or fluid may be supplied from an external source. In the illustrated example the print head 222 has a single row 228 of nozzles 227, but in other examples of print heads more than one row of nozzles may be provided with nozzles offset in one or two dimensions. The diameter of the orifices of nozzles 227 is typically between  $20\mu\text{m}$  and  $50\mu\text{m}$ , and drop diameters are similar. The space or pitch between adjacent nozzle orifices is typically between  $100\mu\text{m}$  and  $500\mu\text{m}$ .

Figure 3a shows a conventional printing strategy in which print head 222 prints successive swathes 302, 304 in the Y-direction, stepping in the X-direction between each swathe. The technique illustrated in Figure 3b may be employed to produce a finer dot pitch. The print head is positioned at an angle  $\Phi$  to the X-direction to reduce the dot pitch by a factor of  $\cos \Phi$ . Figure 3c shows two examples 306 and 308 of the distribution of drop volume ejected from nozzles 227 across the width of print head 222. Generally the size or volume distribution of drops is non-uniform, increasing or falling off at nozzles at the edge of the print head (that is, near an end of a row of nozzles), and further non-uniformity arises from variations in drive efficiency between elements within the print head. Figure 3c shows variations in drop volume, but in general similar variations are also observed in drop velocity. This problem is sometimes addressed in conventional ink jet printing by interlacing the swathes 302, 304.

When depositing materials for molecular electronic devices such as OLEDs, there is a need for both high resolution, generally than better than that required for the best high

resolution graphics, and accurate control of the volume of material deposited, which implies accurate control of "ink" drop volume. Preferably drop volume should be consistent across a print head to perhaps 1 or 2%, and controllable to a few percent. For graphics applications it is drop placement rather than drop volume which is significant and volume variations of 5 to 10% are acceptable. However when constructing molecular electronic devices it is drop volume which is important since this will determine the eventual film thickness which, for an OLED, impacts upon brightness and hence drive current and device lifetime. Thus it is desirable to achieve a volume variation of better than 2%, preferably better than 1%, across an entire OLED display.

To deposit a molecular electronic material a volatile solvent is employed with 1-2% dissolved solvent material. This results in a relatively thin film in comparison with the initial "ink" volume. The drying time is dependent upon the solvent mix and the atmosphere above the substrate, but typically varies between a few seconds and some minutes. It is strongly preferable all the drops comprising material which are eventually to make up a pixel are deposited before drying begins. Solvents which may be used include alkylated benzenes, in particular toluene or xylene. Other solvents for inkjet printing are described in WO 00/59267, WO 01/16251 and WO 02/18513.

The pattern of material to be deposited is made up of pixels formed by depositing the electroluminescent material into a well (as described, for example, in EP 0 880 303) on a substrate. The wells are usually formed by photolithography of a photoresist as described in EP 0 862 156 to which reference may be made. In the case of OLEDs and other molecular electronic devices such as polymer FETs (Field Effect Transistors) these pixels and wells generally have regular shapes and a regular pattern, but in other cases the pixels can have irregular shapes. The substrate typically comprises a substantially non-absorbent material such as, for OLED displays, glass, clear plastics such as polyethylene or PET or other materials such as polyvinylidene fluoride or polyimide. In an OLED display the pixels are typically around 30 $\mu$ m to 50 $\mu$ m across the widest dimension (in a variety of shapes) in a colour display or approximately three times the area in a monochrome display. The gap between the pixels is typically 10-20 $\mu$ m. By contrast the print head is typically around 1cm wide and a few centimetres long.



One known strategy for more accurately controlling the volume of material deposited is to cover a pixel or fill a well using a plurality of sequentially deposited drops rather than a single drop, and this strategy is described in EP '980, in which the print head makes multiple passes in the Y-direction (referring to Figure 3a), depositing one drop onto a pixel on each pass. However this has the disadvantage that there is a relatively long period between successive drops landing on a single pixel, which can result in the "coffee ring" problem illustrated in Figure 4. Furthermore because a zig-zag scanning strategy is adopted for the X-direction the intervals between successive drops landing is non-uniform, depending upon the position of a pixel in the X-direction. With the technique described in EP '980 a slow drying solvent must be employed to prevent drying between successive swathes, but a greater flexibility in solvent choice is preferable and for some applications relatively quick drying solvents such as toluene and xylene, for example with drop drying times of the order of one second, are useful. The technique of EP '980 is directed towards averaging out drop landing errors (thus reducing "banding") as much as averaging out drop volume variations.

Figure 4 illustrates an effect which arises if one drop begins to dry before another is deposited. As the solvent begins to evaporate from drop 400 solvent flows in a direction indicated by arrows 402 because the edge 404 of the drop tends to remain pinned to substrate 406. This results, after a period, in drop shape 410 and the dissolved material tends to be deposited in a ring rather than uniformly. The Applicant's publication WO 02/69119 describes this effect in more detail, and a method of overcoming it by selection of a solvent blend.

Another effect which can arise when depositing materials for molecular electronic devices is known as "tail hooking". Figure 5 shows a drop 500 exiting from an orifice or nozzle 502 of a nozzle plate 504 and illustrates the development of "tail hooking". The drop will eventually break off along dashed line 506 leaving a small amount of dissolved material to drain back into the nozzle orifice before another drop is ejected from the orifice. If sufficient time is not allowed for this process material tends to build up on one side of a nozzle, and this material tends to capture or hook an exiting drop causing the drop to travel at an angle to the desired path. The "dehooking" time

depends upon the fluid properties of the solution comprising the drop and upon dewetting properties of the nozzle plate and for organic polymers for OLEDs dissolved at 1 to 3% may be one or a few milliseconds.

One technique for drop volume control is to calibrate one, or preferably a plurality of nozzles of a printhead by measuring the volume of an ejected drop for a range of printhead drive signals. Data collected in this way may then be used to determine or adjust a printhead drive signal in order to obtain a desired drop volume. Such a calibration procedure may be performed as part of a commissioning process for ink jet or droplet-based deposition apparatus, or a calibration procedure may be performed by the apparatus at switch on.

A problem with such a calibration procedure is the difficulty in obtaining an accurate determination of the volume of an ejected droplet of dissolved material. Figure 6 shows (not to scale) equipment 600 which may be employed to determine the volume of a droplet of dissolved material ejected from a droplet deposition head 602 of droplet deposition apparatus, such as ink jet print head of an ink jet-type printer. In Figure 6 a droplet 606 of dissolved material has been ejected from a nozzle 604 of print head 602 and is in flight towards a substrate 608. Whilst droplet 606 is in flight it is illuminated from an illumination source 610, for example comprising a strobed LED (Light Emitting Diode) 612 and a lens 614. Illumination is directed at droplet 606 by means of a beam splitter 616 and droplet 606 is viewed through beam splitter 616 by a digital camera 618 capable of capturing a high resolution image of the droplet 606 in flight.

Equipment 600 is controlled by a general purpose computer system 620 such as a personal computer into which have been installed a number of interface cards. A print head drive card 620a interfaces with print head 602 and preferably allows the print head to be driven under similar conditions to those encountered during actual operation of the deposition process. A GPIB (General Purpose Instrumentation Bus) interface card 620b drives a power supply 613 for strobed LED 612 to provide illumination in synchronism with drive to the print head 602 such that droplet 606 is illuminated during its flight towards substrate 608. An image acquisition card 620c captures digitized image frames from camera 618, and a local area network interface card 620d will usually be present to

interface with other computer systems, such as a printer (deposition) control computer system, to output drop volume measurement and/or calibration data. Equipment 600 is preferably fitted to the ink jet printer to facilitate calibration of the printer under close to operating conditions and at relatively frequent intervals. The skilled person will appreciate that for clarity, other elements of the printer which are generally present, such as X, Y, Z stage control for the print head/substrate have been omitted from Figure 6.

In operation software running on general purpose computer system 620 controls the illumination and camera to capture a relatively high contrast image of a droplet in flight, corresponding to a known print head drive signal. The print head drive signal typically comprises a unipolar or bipolar pulse drive, comprising a current pulse for a thermal (resistor-based) print head or a voltage pulse for a print head in which droplet ejection is driven by a piezoelectric transducer. Once an image of an ejected droplet has been captured the volume of the droplet is determined by measuring the area or perimeter of the drop, assuming that the drop is spherical. In other arrangements two cameras may be employed to capture images of a droplet from two directions, preferably 90 degrees apart. Other illumination arrangements, such as fibre optic illumination, may also be employed.

In practice there are a number of difficulties in determining an accurate volume of a droplet in flight using the apparatus of Figure 6. The droplet is relatively small and is moving quickly (generally at several metres per second), and it is also difficult to provide good, even illumination. This results in a small depth of field for camera 618, which can result in out of focus images, particularly if the droplet is deviating as it leaves the nozzle. In practice it is also difficult to obtain a desired image contrast. Furthermore, the inks used in this type of printing exhibit considerable visco-elasticity as they leave the nozzle, resulting in droplets with long tails. These tails eventually snap off, part of the tail returning to the nozzle but the majority bouncing forward to catch up the main droplet. This it does in a complex, elastic fashion, often resulting in the formation (perhaps temporary) of sub droplets or satellites. The completed droplets are not necessarily spherical (as assumed) and these cumulative errors in droplet area

measurement are then scaled up (by an additional power of length) when the volume of the droplet is determined.

Further details of drop volume measurement techniques and apparatus may be found in International application number PCT/US02/17369 filed on 31 May 2002 by Litrex Corporation et al., specifically paragraphs 58 to 62, which are hereby incorporated by reference. Also incorporated by reference are the contents of United States Provisional Patent Application Serial No. 60/295,118, entitled "Formation of Microstructures Using Piezo Deposition of Liquid Onto Substrate," filed June 1, 2001, and United States Provisional Application Serial No. 60/295,100, entitled Formation of Printed Circuit Board Structures Using Piezo Deposition of Liquid Onto Substrate, filed June 1, 2001.

When a print head is used to deposit a solution of material for fabricating an organic light emitting diode (OLED) it is also observed that faster droplets tend to have the longest tails, which makes an accurate determination of their volume difficult. Slower droplets tend to be more spherical so that once their area has been measured the presumption of a spherical shape, upon which a volume determination is predicated, is more likely to be correct, but it is more difficult to accurately measure the area of a smaller droplet in the first place. In practice the Applicants have tended to characterize a print head nozzle using relatively low level print head drive signals to provide relatively slow ejected droplets, and a graph of droplet volume against (usually) voltage drive has then been linearly extrapolated to larger level print head drive signals. One possibility is to characterize one nozzle of the print head and then to assume that the same voltage-droplet volume function applies for all the nozzles.

It will be recognized from the foregoing discussion that improved methods of drop volume measurements, for example for print head calibration and/or drive level adjustment/correction, are desirable.

According to a first aspect of the present invention there is therefore provided a method of determining the volume of a droplet of fluid ejected from an orifice of a print head of an ink jet-type printing apparatus, the method comprising: controlling said print head to eject a plurality of droplets from said orifice such that said droplets combine in flight to

form a single, larger droplet; measuring a parameter of said larger droplet from which the volume of said larger droplet may be determined; and determining a volume of one of said plurality of ejected droplets using said parameter.

The measured parameter may comprise, for example, a perimeter or area of the larger drop from which the volume of the larger drop may be calculated although, as the skilled person will recognize, an explicit determination of the volume of the larger drop need not be made.

Ejecting a plurality of what might be termed “sub-droplets” in such a manner that they coalesce to form a single, larger droplet provides a number of volume measurement-related advantages. In embodiments, for example, it is possible to obtain relatively large droplets of dissolved OLED material without the long tails which have previously been observed, and this in turn facilitates measuring the droplet area (or perimeter) and hence facilitates a more accurate determination of volume. The larger droplet also has a more advantageous surface area to volume ratio for the determination of volume from the area (or perimeter) as measured by the camera and software. The larger droplet is also more likely to travel in a straight line, which facilitates positioning the focal plane of a camera, such as the above-described camera 618, for observing the droplet. Furthermore since the single, larger droplet is formed of a plurality of smaller droplets, thermal and other effects which can distort individual droplet sizes tend to average out so, providing a more accurate indication of the volume of a droplet that can be expected for a given drive signal level when the print head is in use for actual deposition of, for example, dissolved molecular electronic material. (Previously, thermal effects have resulted in a “first drop” ejected by a print head nozzle being of a different size to subsequently ejected drops).

For these reasons the calibration and any consequent corrections to the print head drive waveform, tends to be more accurate. In embodiments the volume of one of the plurality of droplets making up the larger droplet is preferably determined by averaging, for example by dividing by the number of ejected (smaller) droplets, and in itself this process tends to reduce measurement error effects.

The print head may be controlled to eject a plurality of droplets, such that they coalesce into a single larger droplet, in a number of ways. For example, with a relatively small spacing between droplets (as determined by experiment for a given print head) one droplet will tend to catch another up because the front droplet will tend to be slowed by air resistance. Alternatively the print head may be driven with a train of pulses such that each successive droplet does not quite break off from the print head before another droplet is ejected (as described, for example, in US 4,503,444). In another method a relatively low level drive signal may be applied to eject a first droplet and successively larger drive signals applied to eject subsequent droplets so that each subsequent droplet is ejected with greater velocity than a preceding droplet (as described, for example, in US 5,285,215). In this way later droplets are traveling faster than a first ejected droplet and thus catch up and coalesce with the first droplet.

In another aspect the invention provides a method of calibrating a print head of an ink jet-type printing apparatus, the method comprising: applying an electrical drive to said print head to eject a plurality of droplets from at least one orifice of said print head such that said droplets combine in flight to form a single, larger droplet; determining an average volume of one of said plurality of droplets ejected from said orifice of said print head by said electrical drive by measuring said larger droplet; and repeating said applying and determining to calibrate said print head.

The electrical drive to the print head may be known, for example because it is accurately controllable by a drive system, or the electrical drive may be measured. The determined average volume may be stored together with data defining or specifying the electrical drive to provide calibration data for the print head. This calibration data may be used to determine an electrical drive to be applied to the print head during use, or it may be used to determine a correction to be applied to an electrical drive. Preferably the calibration method is applied to a plurality of orifices or nozzles of the print head, for example at nozzles at either end and in the middle of the print head, since the electrical drive-drop volume characteristic may vary across printers. This plurality of orifices may be calibrated sequentially or in parallel.

The invention also provides a method of calibrating a droplet deposition head of a droplet deposition apparatus, the method comprising: controlling said droplet deposition head to emit a plurality of smaller droplets such that said plurality of droplets coalesces in flight into a larger droplet; measuring a characteristic of said larger droplet; determining a volume of said larger droplet using a result of said measuring; determining a volume of a said smaller droplet using said larger droplet volume; and calibrating said deposition head using said smaller droplet volume.

The invention also provides a method of depositing material for fabrication of an organic light emitting diode onto a substrate by means of an ink jet-type printing process, said material being dissolved in a solvent, said printing process being adapted for droplet-based deposition of said solvent onto said substrate, the method comprising: positioning said substrate adjacent a droplet-based deposition head for said printing process; moving said deposition head and said substrate relative to one another such that said deposition head is positioned for depositing said dissolved material onto said substrate as a series of pixels; and controlling said droplet-based deposition head for said printing process to eject a series of droplets of said dissolved material in such a manner that said droplets substantially coalesce in flight towards said substrate to form a larger droplet for deposition onto a said pixel.

This deposition technique also provides useful advantages. Broadly speaking because a larger droplet, and preferably a substantially complete volume of material to be deposited on a said pixel, is provided to a pixel (or well) at one time problems associated with solvent drying between successively deposited smaller droplets are alleviated. Furthermore the volume deposited by the larger droplet comprises an averaged out volume of a number of smaller droplets, thus alleviating the "different sized first drop" problem mentioned above and assisting deposition volume accuracy and, in embodiments, repeatability. A further advantage for some applications of the above method is that the larger, combined drop is more likely to travel in a desired direction, particularly because random effects associated with tail breakoff of the "sub-droplets" from the nozzle tend to average out when the sub-droplets combine to form a single larger droplet.

In a still further aspect the invention provides apparatus for determining the volume of a droplet of fluid ejected from an orifice of a print head of an ink jet-type printing apparatus, the apparatus comprising: means for controlling said print head to eject a plurality of droplets from said orifice such that said droplets combine in flight to form a single, larger droplet; means for determining the volume of said larger droplet by measuring said larger droplet; means for determining the volume of one of said plurality of ejected droplets using said determined volume of said larger droplet.

The above-described methods and apparatus may be implemented using processor control code such as conventional program code or code for setting up or controlling an ASIC (Application Specific Integrated Circuit) or FPGA (Field Programmable Gate Array). This processor control code may be provided on a carrier medium such as a hard or floppy disk, CD- or DVD-ROM, programmed memory such as read only memory (Firmware), or on a data carrier such as an optical or electrical signal carrier. As the skilled person will appreciate such code may be distributed between a plurality of coupled components in communication with one another, for example across a network.

These and other aspects of the invention can now be further described, by way of example only, with reference to the accompanying figures in which:

Figures 1a and 1b show, respectively, cross sections through organic light emitting diode and a passive matrix OLED display;

Figures 2a and 2b show, respectively, an ink jet printer and an ink jet printer head;

Figures 3a to 3c show, respectively, conventional swathe printing, skewed printing for reduced dot pitch, and typical ink jet drop volume variations across a print head;

Figure 4 shows drop drying with edge pinning;

Figure 5 shows a cross-section through a nozzle plate illustrating development of tail hooking;



Figure 6 shows apparatus for measuring the volume of an ejected droplet of dissolved material during flight;

Figure 7 shows a known technique for ejecting droplets such that they coalesce during flight;

Figure 8 shows a known print head drive waveform for ejecting droplets so that they coalesce during flight;

Figure 9 shows apparatus for drop volume measurement in accordance with an embodiment of the present invention;

Figure 10 shows a general purpose computer system configured for implementing a droplet volume measurement and print head calibration in accordance with an embodiment of an aspect of the present invention; and

Figure 11 shows a flow diagram of a calibration procedure including a drop volume measurement process according to an embodiment of the present invention.

Figure 7, which is taken from US 4,503,444, shows one technique for ejecting a plurality of droplets such that they coalesce in flight. A packet of drive pulses is applied to the print head (in the example described in US '444, a thermally-driven print head), each (current) pulse in the packet causing the emission of a single droplet. The packet of pulses thus causes the print head to eject a "packet" of droplets, and providing the interval between individual pulses is short enough for the droplet not to individually break off from the ink jet orifice, the individual droplet within the packet remain connected and merge in flight to form a single, larger droplet. (In the case of the thermal print head described in US '444 the interval between individual pulses should also be long enough to ensure that bubble collapse occurs after the application of each pulse).

Referring to Figure 7 a print head orifice 700 emits a first droplet 702 and a short time later a second droplet 704. Figure 7 shows a set of twelve illustrations showing how these droplets merge overtime to create a single, larger droplet 706. Packets of from 0 to N pulses may be used to cause the emission of drops comprising from 0 to N droplets. The pulse packet parameters (pulse amplitude, width and spacing) depend upon the print head and upon the ejected fluid and may be determined by routine experiment. The object of US '444 is to create a printed grey scale; for further details reference may be made to this specification.

A second technique for ejecting droplets such that they coalesce in flight (or upon striking a substrate) is described in US 5,285,215. This technique is described in the context of a drop-on-demand ink jet print head employing a piezoelectric transducer. The technique described in US '215 also involves applying a succession of pulses to the print head, but these pulses have differing amplitudes and/or pulse widths such that the ejected droplets have differing amplitudes and/or pulse widths such that the ejected droplets have different velocities, and more particularly such that successively ejected droplets are ejected at successively increased speeds so that they catch one another up whilst airborne and merged together.

Figure 8, which is taken from US '215, shows an example of a print head drive waveform for ejecting three droplets, a first pulse 11 ejecting a first droplet, a second pulse 13 ejecting a second droplet, and a third pulse 15 ejecting a third droplet. Pulse 11 has a first (voltage) amplitude  $+V_1$  and a length (in time)  $T_1$ ; pulse 13 has an amplitude  $+V_2$  and length  $T_2$ ; and pulse 15 has an amplitude  $+V_3$  and a length  $T_3$ .

As described in US '215, in one experiment with a given ink jet device, the inventor of US '215 set the amplitudes of pulses 11, 13, 15 to 30 volts ( $+V_1$ ,  $+V_2$  and  $+V_3$  all equal 30 volts), with pulses 11, 13 and 15 typically having exponential fall times of 10 microseconds, 5 microseconds and 1 microsecond, respectively; and pulse widths of 60 microseconds, 40 microseconds and 30 microseconds, respectively. When applied to a selected transducer of an ink jet print head, pulse 11 caused a first ink droplet to be ejected, pulse 13 caused a second ink droplet of greater velocity than the first to be ejected, and pulse 15 caused a third ink droplet of even greater velocity to be ejected,

whereby all of these ink droplets were of such relative velocities that they merged in flight prior to striking a recording media.

Either a pulse amplitude or a pulse length or a pulse shape (for example rise and/or fall time), or a combination of two or more of these may be varied to vary the ejection velocity of a droplet. As before, the particular parameters required for a given combination of print head and deposited material may be determined by routine experiment. The object of US '215 is to control the boldness of printing by controlling printed dot size.

Referring now to Figure 9, this shows apparatus 900 configured to employ the above-described techniques to measure the volume of a droplet of material ejected from a print head of ink jet printing-type apparatus by measuring the volume of a larger, coalesced droplet made of a plurality of smaller "sub-droplets". Broadly speaking the apparatus of Figure 9 is similar to that shown in Figure 6 and like elements are denoted by like reference numerals. The main difference is the software 902 running on general purpose computer 620. This software includes print head driver code 902a, illumination control code 902b, image capture and analysis code 902c, and volume determination code 902d.

Print head 602 may be either a thermal or piezoelectrically-driven print head. Examples are the XJ126, XJ128 and XJ500 print heads available from Xaar of Cambridge, UK and the Litrex 80L print head, for use with the Litrex 80L Piezo Micro Deposition (PMD) System (Trade Mark), from Litrex Corporation of Pleasanton, California. The Litrex System is particularly suitable for the deposition of light emitting polymers. The print head 902 is loaded with dissolved material such as material for a molecular electronic device, for example an OLED-based display. The print head driver 902 then controls head drive card 620a to eject a plurality of droplets 904a, b, c from one or more orifices 604 of the print head. These smaller droplets gradually catch one another up, and apparatus 900 is arranged such that the droplets have sufficient flight distance to coalesce into a single, larger droplet 906 and, preferably to allow a small time interval for this larger droplet to settle into an approximately spherical shape. (For convenience

smaller droplets 904 and larger droplets 906 are shown present at the same time in Figure 9).

The technique described with reference to Figure 7 or Figure 8 above may be employed to ensure that the drops coalesce. Alternatively, provided that flight distance is sufficient, and the spacing between the smaller droplets 904 is not too large, the smaller droplets 904 will merge without the use of any special techniques because of the effects of air resistance slowing the first drop down more than the following drops. Again the determination of drop size/separation and flight distance to achieve this is a matter for routine experimentation.

The illumination control software 902b is synchronised with the print head drive to control the illumination 612 to illuminate the single, larger droplet 906 after the smaller droplets 904 have merged, and substrate 608, beam splitter 616 and camera 618 are positioned accordingly. Likewise image capture and analysis code 902c is also synchronised with the print head drive and illumination control to capture and store a digitised image from the camera when droplet 906 is illuminated.

The image analysis portion of code 902c locates the edge of the captured, digitised image of the droplet and then measures the perimeter and/or area of the droplet. As the skilled person will be aware there are many suitable commercial image processing packages which may be employed for such a purpose, for example MATLAB software from MathWorks, Inc., MA, USA.

Once the perimeter and/or area of the larger drop 906 has been measured the volume of this larger drop may be determined and hence, knowing the number of smaller drops that the print head was driven to provide, an average volume for one of the smaller droplets can be determined. Any number of smaller droplets may be merged to form the larger droplet but, in general, more accurate volume measurements will result from combining a larger number of droplets, within practical limitations. The print head 602 is preferably (but not necessarily) driven with the aim of ejecting a series of smaller droplets of substantially the same volume. Thus if, for example, a drive waveform of the type shown in Figure 8 is employed the parameters of each pulse are preferably

selected such that each ejected droplet is intended to have substantially the same volume, albeit a different velocity.

The average volume of a smaller droplet may straightforwardly be determined using the following equations:

From a measured area,  $A = \pi R^2$  of a larger droplet of radius  $R$ , a volume  $V$  of the larger droplet may be determined from:

$$V = (4/3) \pi R^3 = (4/3) \pi^{-1/2} A^{3/2}$$

From a measured perimeter  $P = 2\pi R$  of a larger droplet of radius  $R$ , a volume  $V$  of the larger droplet may be determined from:

$$V = (4/3) \pi R^3 = P^3 / (6\pi^2)$$

If  $n$  smaller droplets coalesce to form this larger droplet an average volume  $v$  of such a smaller droplet is then given by:

$$v = V/n = (1/n) (4/3) \pi^{-1/2} A^{3/2} \quad \text{or} \quad (1/n) P^3 / (6\pi^2).$$

In this way the volume of a smaller droplet may be determined with greater accuracy than with previously employed techniques. Such a volume measurement may also be used as a basis of a calibration procedure for an ink jet-type printing apparatus, as described in more detail below with reference to Figure 11.

The above described multiple-droplet ejection technique may also be employed for depositing dissolved material for a molecular electronic device along the lines described above. Thus by driving the print head to eject a plurality of smaller droplets such that these droplets coalesce in flight to form a single, larger droplet more accurate control of the deposited volume is possible. Furthermore, depositing a single, larger droplet rather than a series of smaller droplets, at different times and often spaced apart by long intervals alleviates problems such as the above-described coffee-ring effect. Such a

multiple drop ejection technique also enables more accurate positioning of deposited drops of dissolved material, which is important for the very high resolution printing needed for "ink jet" printing of molecular electronic devices such as OLEDs. This is because directional variations in ejected droplets due to tail hooking are reduced. When printing apparatus (such as the apparatus outlined in Figure 9) is operated in this way the distance between the print head 602 and substrate 608 may need to be increased as compared with conventional techniques in order to provide room for the smaller drops to coalesce as otherwise, in some instances, deposition can occur with a drop or chain of drops bridging the nozzle plate of the print head and the substrate. Successful deposition has, in other cases, also been achieved with such bridging occurring.

Figure 10 shows details of a general purpose computer system 1000, similar to the general purpose computer 620 of Figure 9, suitable for implementing the above-described methods.

Referring to Figure 10, the computer system 1000 includes a data and control bus 1002 to which are connected a processor 1012, working memory 1014, data memory 1016, programme memory 1018, a keyboard and pointing device 1008, and a display 1010 for providing a user interface. Also coupled to bus 1002 are a network interface device 1006 for interfacing to a local area network for exchange of data such as deposition data files, a print head drive card 1020, a print head X-Y motion control and ancillary control card 1022, an illumination control card 1024 and an image capture card 1026. Data in program memory 1018 and/or data memory 1016 may be written to and/or read from portable storage media, illustratively shown by floppy disk 1004.

The print head drive circuitry 1020 provides an electrical drive to the print head via a serial or parallel bus within umbilical 204 of Figure 2a, to control drop ejection from the print head. The X-Y and ancillary motion control card 1022 also connects to umbilical 204 to provide X-Y drive control signals, for example to stepper motors, optionally to receive feedback, for example from shaft encoders, and to provide ancillary control functions, for example position detection/calibration and Z-direction head motion control. Card 1024 drives the strobed illumination and card 1026 controls

the digital camera to capture an image, and receives and stores the captured image. In alternative embodiments cards 1020 to 1026 may comprise separate hardware.

Permanent program memory 1018 includes calibration control code to control a print head calibration process, print head drive code to drive the print head with a pulse train to produce a corresponding train of ejected droplets, image capture and analysis code for interfacing with camera 618 of Figure 9 and for analysing captured data, drop volume determination code for determining the volume of a coalesced droplet and an average volume of a smaller droplet, optional interpolation/extrapolation code to interpolate between and/or extrapolate from calibration data points, optional operator interface code to provide a user interface, and operating system code including code, for example, to control head-substrate position, droplet deposition control code, and code for saving/loading/communicating calibration data. Processor 1012 loads and implements this code to provide the corresponding functions. Working memory 1014 is used by processor 1012 for temporary calculations for this purpose. Non-volatile data memory 1016 stores data such as a calibration specification data file to specify a calibration procedure to be applied to a print head, and a calibrated drive data file to store, for example, drive data in association with measured (calibrated) droplet volumes. Data memory 1016 may also store deposition data specifying a pixel pattern and associated volumes of material to deposit, for example as a deposition map.

Figure 11 shows a flow diagram of a calibration procedure which may be implemented by the computer system 1000 of Figure 10.

The procedure begins at step S1100, at which a data file specifying a calibration procedure to be applied is initialised. This data file may specify, for example, a range of drive signals/droplet volumes over which a print head is to be calibrated and (one, some or all) nozzles of the print head which are to be calibrated. The calibration procedure may be performed automatically from time to time or, for example, when the printing apparatus is first switched on.

At step S1102 data specifying a first calibration point is read from the calibration specification data file. Typically this specifies a desired or requested droplet volume

together with a number of droplets which are to be merged to form a larger droplet on which measurements are to be performed. Then, at step S1104, drive data for driving the print head to produce droplets of this volume is read from a drive data file. This file may, for example, comprise data specifying a drive waveform to be applied to the print head to eject one or the selected number of "sub-droplets" of the desired volume. The drive waveform may comprise either a current or voltage drive, depending upon the type of print head employed. Typically at least a (voltage or current) drive level and a drive time will be specified to define a sub-drop volume and, where necessary, to control a sub-droplet ejection velocity. If, at step S1104, drive data for single sub-drop ejection is read from the drive data file then, at step S1106, drive data to eject a series of such sub-droplets is formed, for example by forming a train of pulses having an appropriate (time) spacing, such that the sub-droplets will coalesce in flight. Thus, for example, a narrowly spaced train of pulses may be employed (as described above) or drive pulses or waveforms may be selected to provide ejected droplets with successively increased ejection velocities but substantially the same droplet volume. For example, if a higher voltage is to be employed, for faster droplet ejection, a shorter pulse may be necessary in order to provide each of the merging sub-drops with substantially the same volume.

Once an appropriate print head drive waveform has been formed the computer system drives the print head with this waveform and, after an appropriate interval to allow the ejected sub-droplets to merge, controls the strobed illumination and camera to capture an image of the larger, merged droplet (step S1108). The captured image is then stored and analysed at step S1110 to determine the volume of the coalesced droplet (although strictly the volume of the coalesced droplet need not explicitly be determined in order to determine the average volume of a sub-droplet). At step S1112 the average sub-droplet volume is determined and this information is written into a calibrated drive data file (which could be the same drive data file that the desired sub-droplet volume was read from in step S1104). In this way drive data specifying a print head drive waveform is associated with measured ejected droplet volume data for the drive waveform. The measured droplet volume data may either be stored explicitly, as a volume ejected by a given drive waveform, or may be stored, for example, as a correction to an estimated or previously measured ejected sub-droplet volume for that drive waveform.



The procedure checks, at step S1114, whether or not the calibration is complete, that is whether or not all the calibration points specified in the calibration specification data file have been measured. If the calibration is not complete the procedure loops back to step S1102 to read the next calibration point from the calibration specification data file, otherwise the procedure continues to step S1116, which interpolates between and extrapolates from the stored calibration data to provide estimated ejected droplet volume data for drive waveforms intermediate between those specified in the calibration specification data file. However, this interpolation/extrapolation procedure is optional. The calibration procedure for a single orifice of the print head is then complete, although the procedure may be repeated for other orifices of the print head. Optionally the procedure may also be repeated for the same orifice using the calibrated drive data stored in step S1112 as an input to the calibration routine, that is as data read in step S1104.

The skilled person will recognise that many variations to the procedure of Figure 11 are possible. For example, image collection may be performed for a series of droplet volumes and then image analysis and volume determination performed in a separate procedure at a later time.

No doubt many other effective alternatives will occur to the skilled person and it will be understood the invention is not limited to the described embodiments and encompasses modifications apparent to those skilled in the art lying within the spirit and scope of the claims appended hereto.

**CLAIMS:**

1. A method of determining the volume of a droplet of fluid ejected from an orifice of a print head of an ink jet-type printing apparatus, the method comprising:  
controlling said print head to eject a plurality of droplets from said orifice such that said droplets combine in flight to form a single, larger droplet;  
measuring a parameter of said larger droplet from which the volume of said larger droplet may be determined; and  
determining a volume of one of said plurality of ejected droplets using said parameter.
2. A method as claimed in claim 1 wherein said measuring of said larger droplet is performed whilst said larger droplet is in flight.
3. A method as claimed in claim 1 or 2 wherein said fluid comprises dissolved material for a molecular electronic device.
4. A method as claimed in any preceding claim wherein said controlling comprises applying a train of electrical pulses to said print head.
5. A method as claimed in any preceding claim wherein said determining of the volume of one of said plurality of ejected droplets comprises determining an average volume of one of said plurality of ejected droplets.
6. A method as claimed in any preceding claim wherein said parameter comprises an image area or perimeter of said larger droplet.
7. A method as claimed in any preceding claim further comprising adjusting a drive to said print head in response to a result of said measuring and determining.
8. A method of calibrating a print head of an ink jet-type printing apparatus, the method comprising:

applying an electrical drive to said print head to eject a plurality of droplets from at least one orifice of said print head such that said droplets combine in flight to form a single, larger droplet;

determining an average volume of one of said plurality of droplets ejected from said orifice of said print head by said electrical drive by measuring said larger droplet; and

repeating said applying and determining to calibrate said print head.

9. A method as claimed in claim 8 comprising applying said electrical drive to eject pluralities of droplets from a plurality of orifices of said print head; determining an average volume of a droplet of each of said pluralities of droplets; and repeating said applying and determining to calibrate said plurality of orifices of said print head.

10. A method as claimed in claim 8 or 9 further comprising storing calibration data derived from said repeated applying and determining for use in modifying an electrical drive to be applied to said print head during use.

11. A method of calibrating a droplet deposition head of a droplet deposition apparatus, the method comprising:

controlling said droplet deposition head to emit a plurality of smaller droplets such that said plurality of droplets coalesces in flight into a larger droplet;

measuring a characteristic of said larger droplet;

determining a volume of said larger droplet using a result of said measuring;

determining a volume of a said smaller droplet using said larger droplet volume;

and

calibrating said deposition head using said smaller droplet volume.

12. A method of depositing material for fabrication of an organic light emitting diode onto a substrate by means of an ink jet-type printing process, said material being dissolved in a solvent, said printing process being adapted for droplet-based deposition of said solvent onto said substrate, the method comprising:

positioning said substrate adjacent a droplet-based deposition head for said printing process;

moving said deposition head and said substrate relative to one another such that said deposition head is positioned for depositing said dissolved material onto said substrate as a series of pixels; and

controlling said droplet-based deposition head for said printing process to eject a series of droplets of said dissolved material in such a manner that said droplets substantially coalesce in flight towards said substrate to form a larger droplet for deposition onto a said pixel.

13. A method as claimed in claim 12 wherein each said pixel is formed from substantially a single said larger droplet.

14. Processor control code to, when running, implement the method of any preceding claim.

15. A carrier carrying the processor control code of claim 14.

16. Apparatus for determining the volume of a droplet of fluid ejected from an orifice of a print head of an ink jet-type printing apparatus, the apparatus comprising:

means for controlling said print head to eject a plurality of droplets from said orifice such that said droplets combine in flight to form a single, larger droplet;

means for determining the volume of said larger droplet by measuring said larger droplet;

means for determining the volume of one of said plurality of ejected droplets using said determined volume of said larger droplet.

**ABSTRACT:****DROPLET - DEPOSITION RELATED METHODS AND APPARATUS**

This invention generally relates to the deposition of material for electronic devices, particularly molecular electronic devices such as organic light emitting diodes, by an ink jet-type process. The invention is particularly concerned with droplet, volume measurement and calibration techniques and deposition methods.

A method of determining the volume of a droplet of fluid ejected from an orifice of a print head of an ink jet-type printing apparatus is described. The method comprises controlling the print head to eject a plurality of droplets from said orifice such that said droplets combine in flight to form a single, larger droplet; determining the volume of said larger droplet by measuring said larger droplet; and determining the volume of one of said plurality of ejected droplets using said determined volume of said larger droplet.

Figure 11

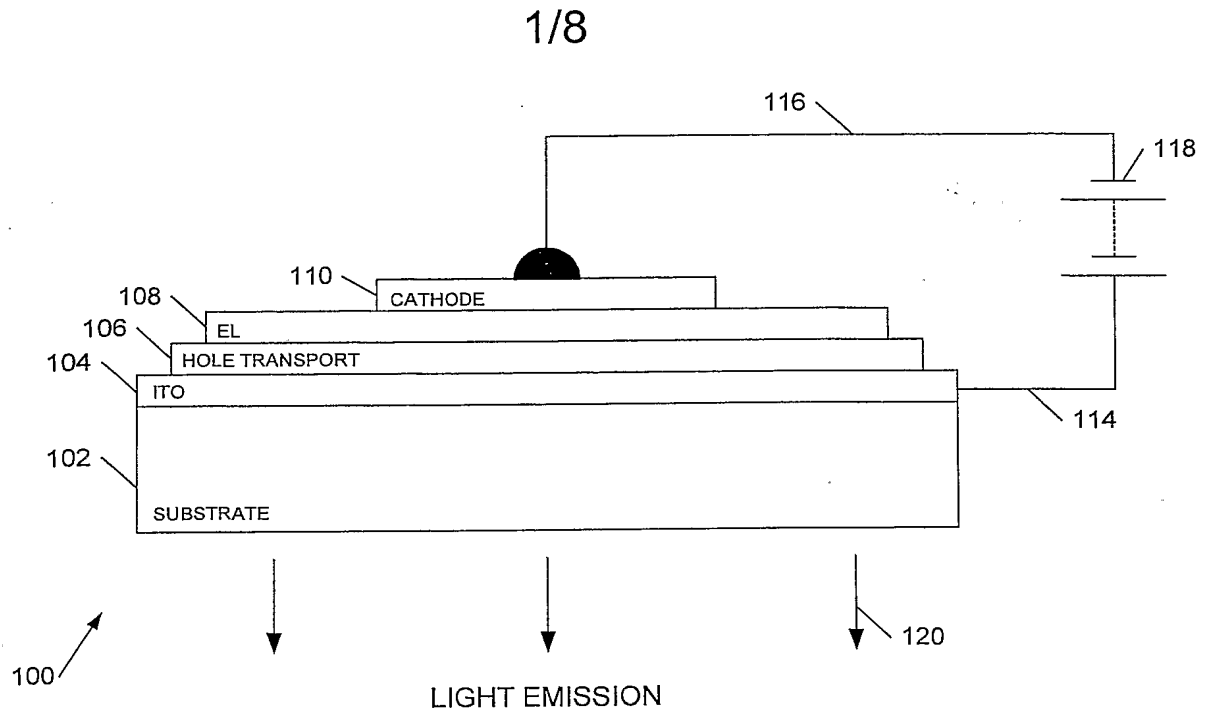


Figure 1a  
(PRIOR ART)

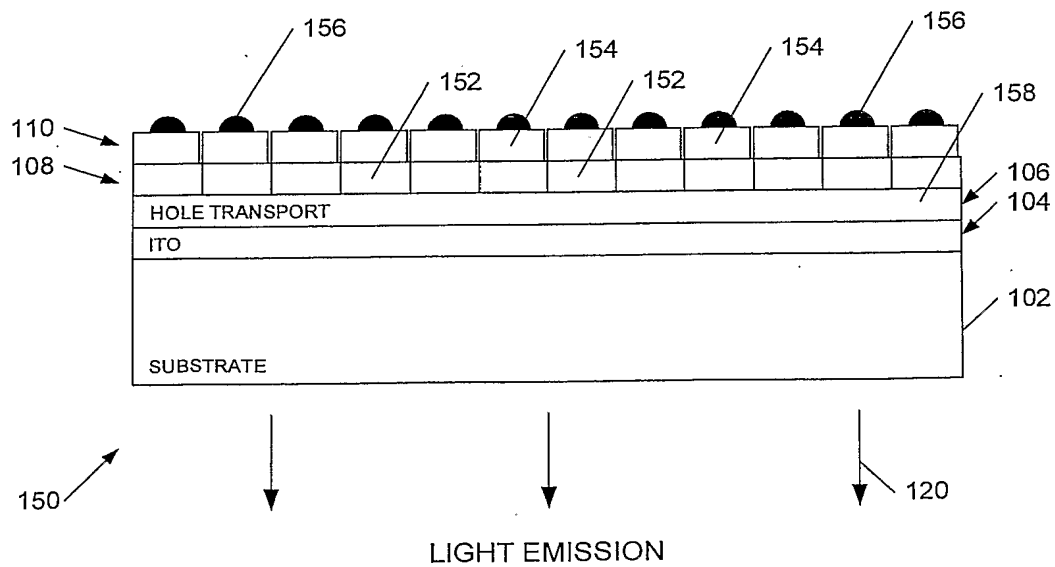


Figure 1b  
(PRIOR ART)

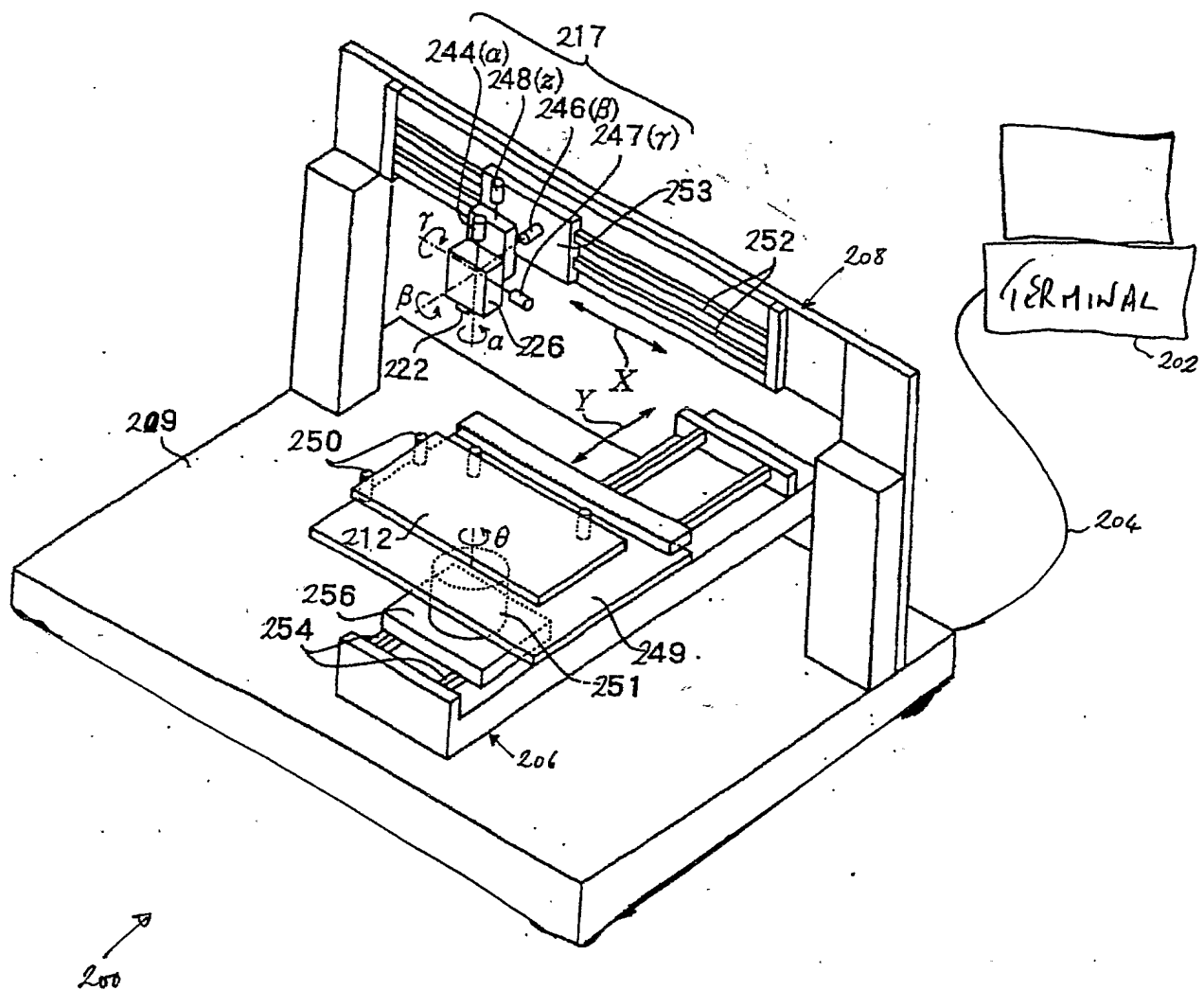


FIGURE 2A

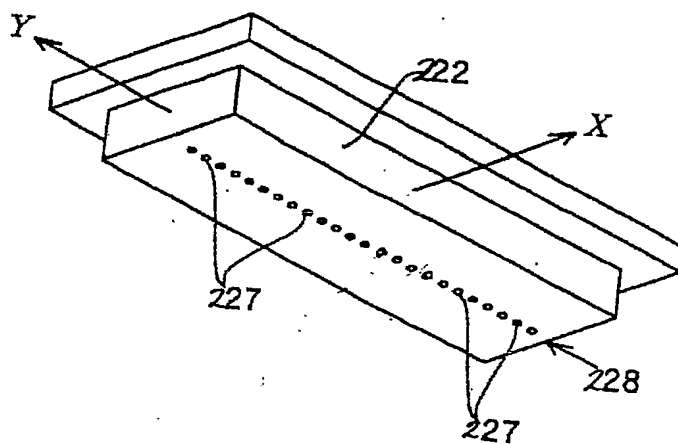


FIGURE 2B

3/8

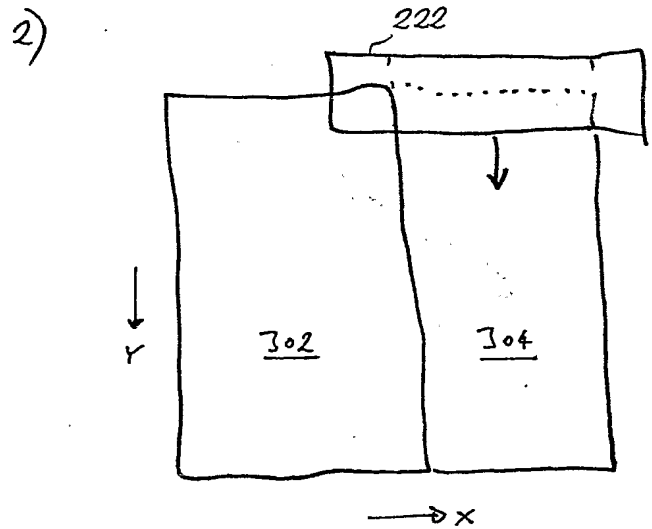
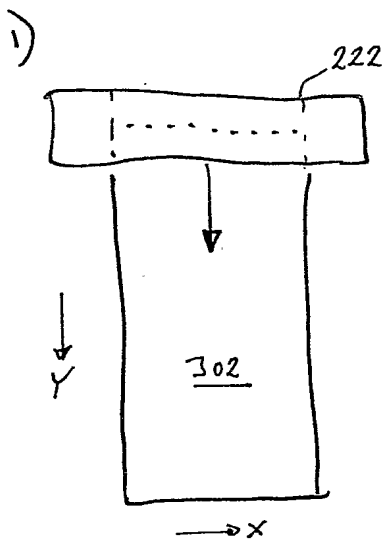


FIGURE 3A

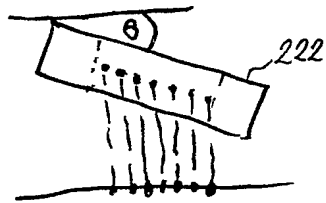


FIGURE 3B

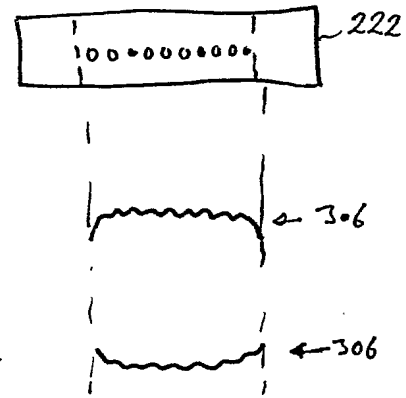


FIGURE 3c

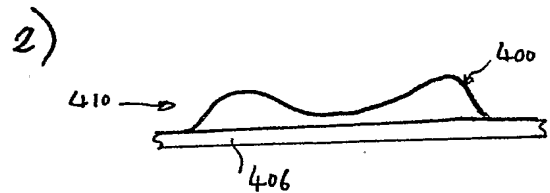
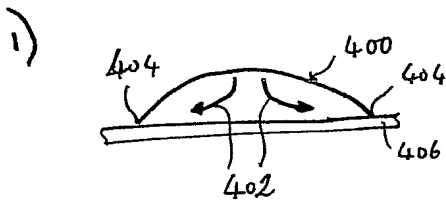


FIGURE 4



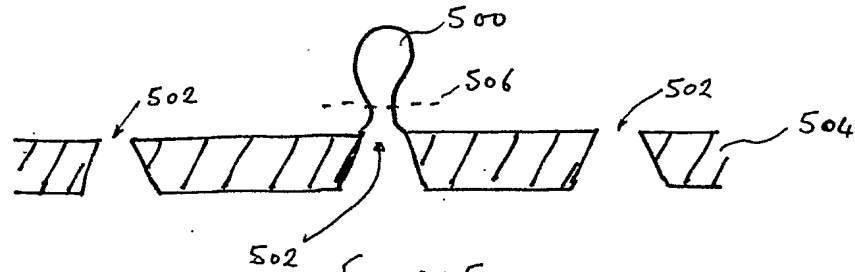


FIGURE 5

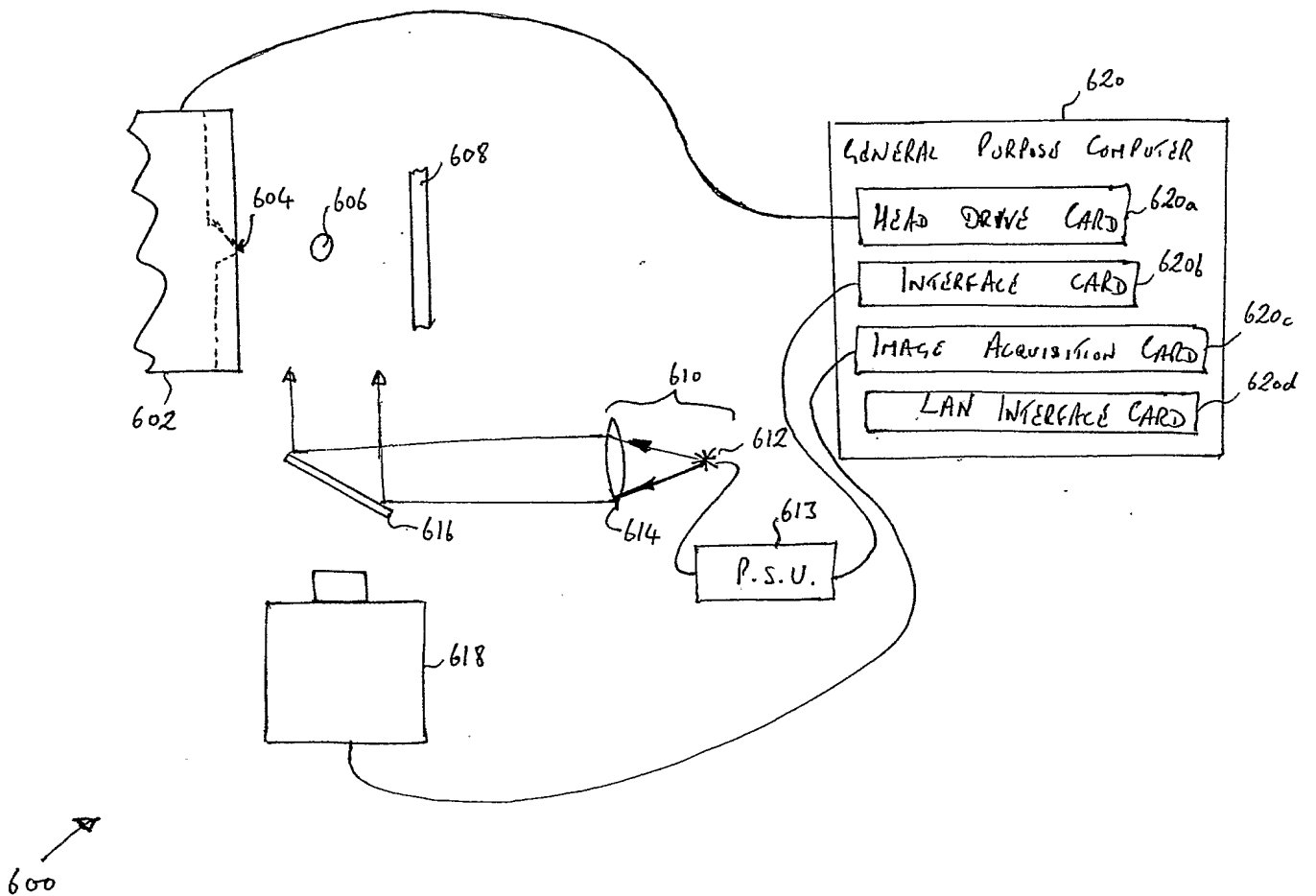


FIGURE 6

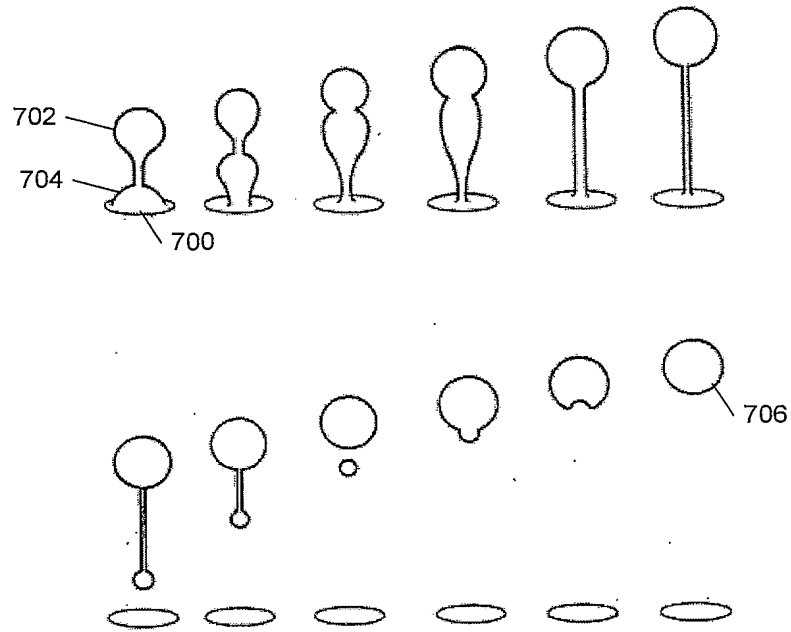


Figure 7  
(PRIOR ART)

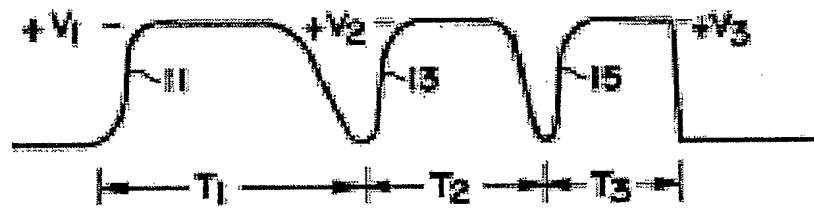


Figure 8  
(PRIOR ART)

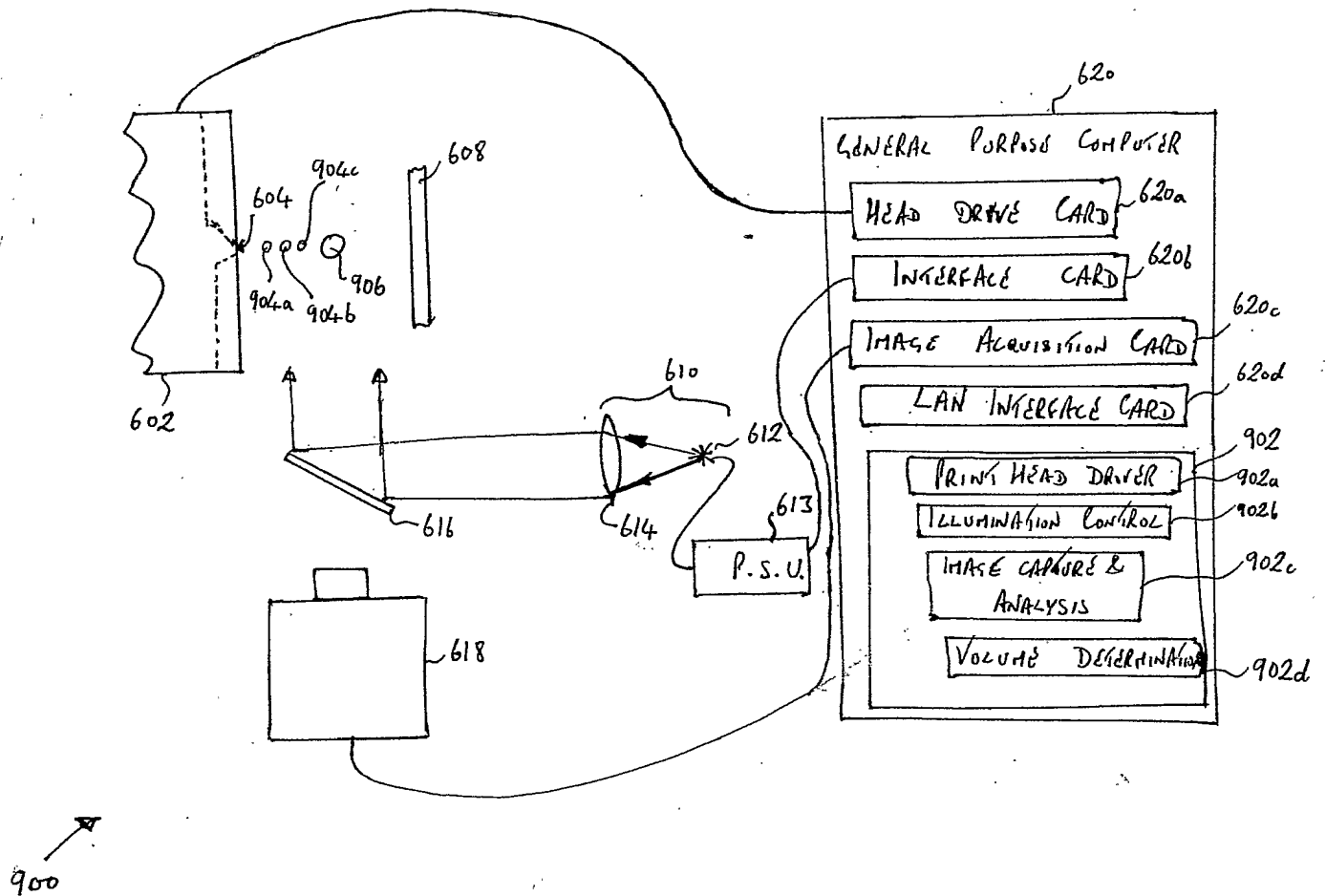


FIGURE 9

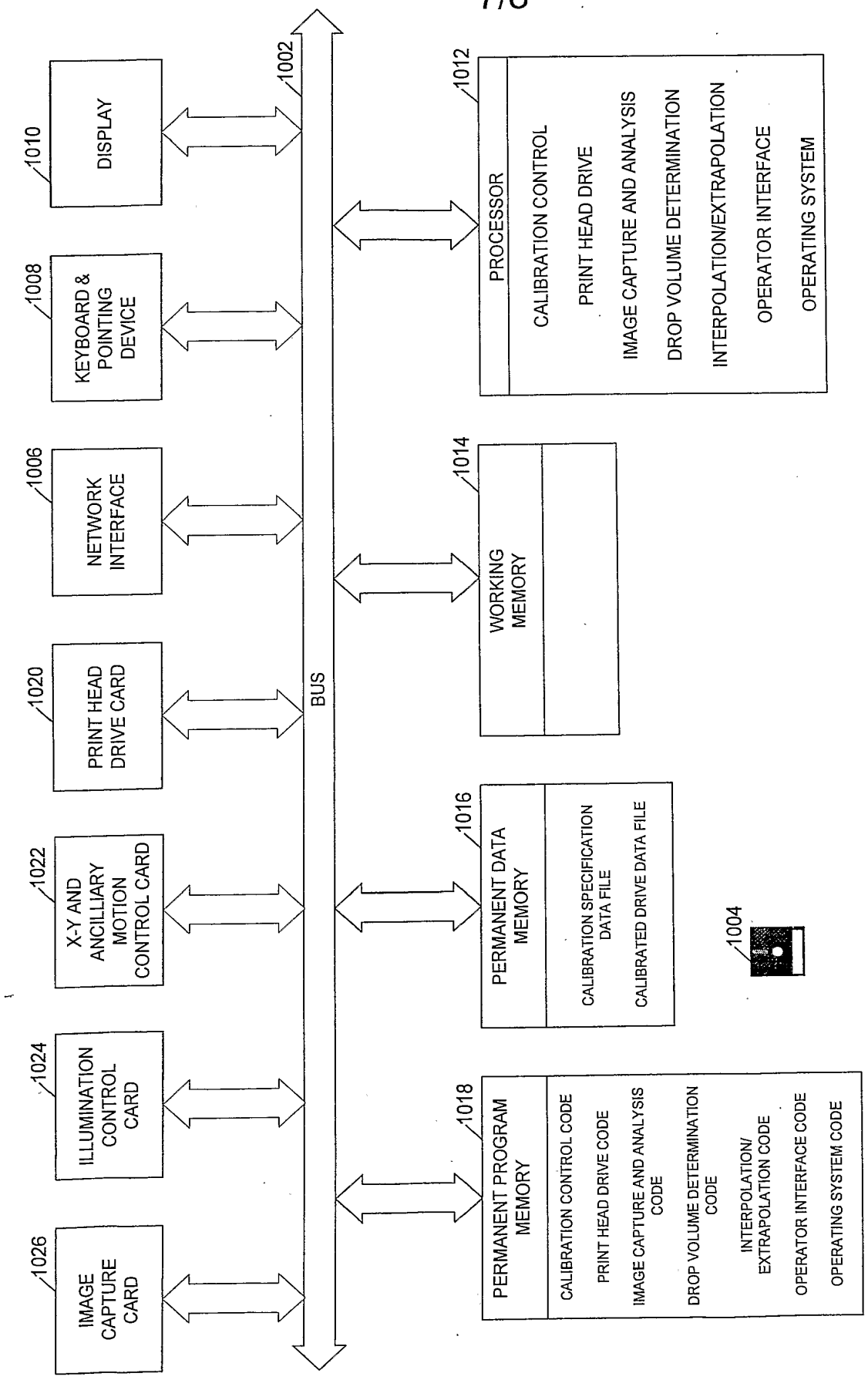


Figure 10

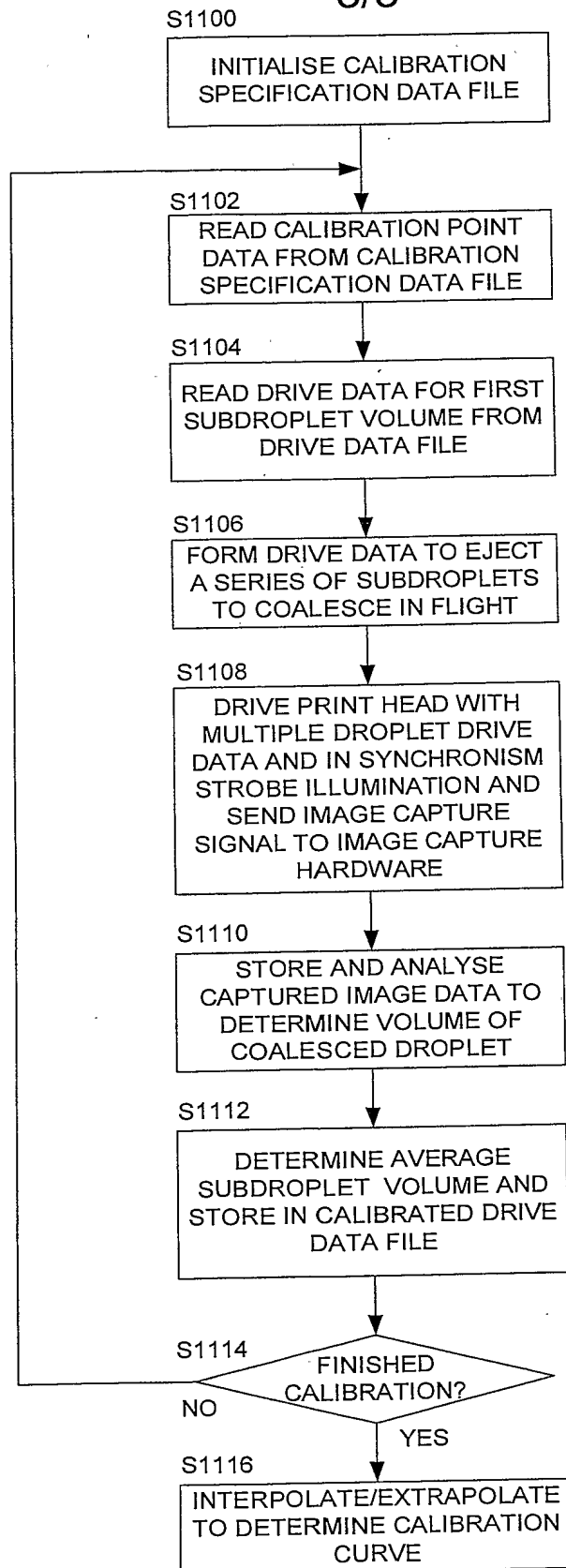


Figure 11

PCT Application  
**GB0305033**

